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# Interplay between spin glass and heavy fermion behavior in the $d$ -metal oxides $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$

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The magnetic relaxation rate of the  $d$ -metal oxide system  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  has been measured on polycrystalline samples for  $x=0.05, 0.1, 0.2$ , and  $0.3$  by means of quasielastic neutron scattering. All investigated compounds display a quasielastic response of magnetic origin with a residual quasielastic line width of  $8\text{--}15$  K followed by a square-root temperature dependence. We argue that the residual linewidth corresponds to the energy scale of antiferromagnetic fluctuations. The main effect of Zn doping is to introduce disorder. This is reflected by the formation of a spin glass state with increasing freezing temperature upon increasing Zn concentration. However, the present data are inconsistent with a spin-glass state alone but give indications of strong hybridization effects. Our present results may be interpreted on the basis of recent band structure calculations.

Among very many different transition metal oxides crystallizing in the fcc spinel structure,  $\text{LiV}_2\text{O}_4$  is one of the three metallic compounds<sup>1</sup> known so far (besides  $\text{LiTi}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ ). No sign of magnetic order or superconductivity could be observed for  $T \geq 0.02$  K.<sup>2</sup>  $\text{LiV}_2\text{O}_4$  is the first example of a  $d$ -metal compound exhibiting heavy-fermion (HF) behavior as has been proposed by Kondo *et al.*<sup>2</sup> on the basis of specific heat, susceptibility, and NMR measurements. Furthermore, an anomalous temperature dependence of the lattice constants and the thermal expansion<sup>3,4</sup> below  $T=20$  K are significant of a strongly enhanced Grüneisen parameter, which again is a characteristic property of HF systems. An alternative explanation of the temperature dependence of the spin-lattice relaxation rate in terms of spin fluctuations close to a ferromagnetic instability has been put forth by Fujiwara *et al.*<sup>5</sup>

Recent muon spin resonance ( $\mu\text{SR}$ ) studies<sup>6</sup> on  $\text{LiV}_2\text{O}_4$  indicated a close relation of the ground state properties of  $\text{LiV}_2\text{O}_4$  to spin glass behavior but without any static freezing in. Measurements of the magnetic relaxation rate of  $\text{LiV}_2\text{O}_4$  by means of quasielastic neutron scattering revealed a residual quasielastic linewidth of  $0.5$  meV and a square root temperature dependence without any significant  $Q$  dependence,<sup>7</sup> characteristic for the formation of a heavy fermion state. Between  $40$  and  $80$  K, the magnetic response of  $\text{LiV}_2\text{O}_4$  changes drastically. For  $T \geq 80$  K a linear  $Q$  dependence develops as it is expected in phenomenological spin fluctuation theories of weak ferromagnetic metals.<sup>8</sup> The magnetic phase diagram of the Zn doped system  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  has been investigated by Ueda *et al.*<sup>9</sup> The inherent geometrical frustration of the spinel structure of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  may easily suppress magnetic order. For pure  $\text{ZnV}_2\text{O}_4$ , a structural phase transition at  $50$  K removes the frustration and subsequently below  $40$  K the compound shows long range antiferromagnetic order.<sup>9</sup> For a large intermediate concentration regime  $0.1 \leq x \leq 0.9$  the magnetic frustration and the alloying induced disorder lead to a spin glass state below  $T_F \approx 10$  K.<sup>9</sup> For  $x \leq 0.1$  no sign of magnetic order could be

observed by means of susceptibility measurements. Increasing the Zn concentration is accompanied by a linear increase of the lattice constant and the unit cell volume, respectively.<sup>9</sup> One therefore might interpret these results as a transition from a nonmagnetic heavy fermion state in  $\text{LiV}_2\text{O}_4$  via an intermediate spin-glass state to antiferromagnetic order in  $\text{ZnV}_2\text{O}_4$ .

Traditionally, in strongly correlated  $f$ -electron systems such a transition has been described within the framework of Doniach's phase diagram.<sup>10</sup> It is based on the competition between magnetic intersite interactions favoring long-range magnetic order and demagnetizing Kondo-like on-site interactions responsible for the formation of a heavy fermion state. Here we report on a systematic neutron scattering study on  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  in order to investigate the evolution of the heavy fermion state in pure  $\text{LiV}_2\text{O}_4$  when expanding the lattice by substituting Li by Zn.

Polycrystalline samples of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  with  $x=0.05, 0.1, 0.2$ , and  $0.3$  have been synthesized by sintering a mixture of powders of  $\text{LiVO}_3$ ,  $\text{VO}$ ,  $\text{VO}_2$ , and  $\text{ZnO}$  with a slight excess of  $\text{LiVO}_3$  in order to compensate for Li evaporation. Platinum crucibles were used for reaction of the powders at  $750^\circ\text{C}$  for 10 days. X-ray diffraction experiments revealed the nominally pure fcc normal spinel structure for all investigated concentrations. No signs of spurious phases could be detected. The lattice constants are in good agreement with the results of Ref. 7. From EPR and magnetic susceptibility measurements we estimate a number of approximately  $0.1\%$  V defects for all compounds.

In inelastic neutron scattering experiments one measures the dynamic structure factor  $S(Q, \omega, T)$  which is related to the imaginary part of the dynamical susceptibility  $\chi''(Q, \omega, T)$  by

$$S(Q, \omega, T) = (1 - e^{-\hbar\omega/k_B T})^{-1} \chi''(Q, \omega, T). \quad (1)$$

In the absence of correlations, a local magnetic moment will give a sharp  $\delta$ -function peak in  $S(Q, \omega, T)$ . Exchange inter-

actions with conduction electrons will yield Lorentzian line shapes and the corresponding width  $\Gamma(Q, T)$  at low temperatures gives a rough estimate of the hybridization strength and determines a characteristic temperature  $T^*$ .

Quasielastic neutron scattering experiments have been performed on the time-of-flight spectrometer IN6 at the Institut Laue Langevin (ILL), Grenoble. The incoming neutron wave length was 5.1 Å. Carefully powdered samples were filled in a flat-plate sample holder and mounted in a cryostat allowing for temperatures  $1.5 \text{ K} \leq T \leq 300 \text{ K}$ . Additionally, a vanadium plate and an empty sample holder have been measured to account for detector efficiency and background signal, respectively. The raw data were corrected in a standard way employing the INX program and subsequently fitted with the PROFIT program (both routines of the ILL). Under the given experimental conditions (available beam time, sample quantities, dynamic structure factor, large incoherent scattering cross section of vanadium, etc.) the resulting counting statistics did not allow for a detailed analysis of the  $Q$  dependence of the scattering. At least, a comparison of the observed quasielastic scattering intensities at low and high  $Q$  values (corresponding to a summation of the detectors for  $10.33^\circ \leq 2\Theta \leq 52.69^\circ$  and  $52.69^\circ \leq 2\Theta \leq 114.0^\circ$ , respectively) showed that these contributions decrease with increasing momentum transfer  $Q$ , thus indicating its magnetic origin.

Phenomenologically, the data could be satisfactorily fitted by a single quasielastic Lorentzian multiplied by the detailed balance factor and convoluted with the instrumental resolution. The corresponding simple relaxational ansatz for the dynamic susceptibility is given by

$$\chi''(Q, \omega, T) = \omega \Gamma(Q, T) \frac{\chi_0(Q, T)}{\omega^2 + \Gamma^2(Q, T)}. \quad (2)$$

$\Gamma(Q)$  is the  $Q$ -dependent half width at half maximum (HWHM) and  $\chi_0(Q, T)$  is related to the bulk susceptibility  $\chi_0(T)$  via the magnetic form factor  $f^2(Q)\chi_0(T)$ . Figure 1 shows the quasielastic scattering intensities for  $x = 0.05, 0.1, 0.2$ , and  $0.3$  at  $T = 15 \text{ K}$ . The data have been fitted according to Eqs. (1) and (2) (solid lines in Fig. 1). The strong increase of the quasielastic intensity around zero energy transfer is due to incoherent elastic scattering contributions. Already a rough inspection of Fig. 1 reveals that at  $T = 15 \text{ K}$ , the magnetic scattering decreases with increasing Zn concentration, despite the fact that the number of V ions remains constant.

Figure 2 shows the temperature dependence of the quasielastic line width of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  for  $x = 0.05, 0.1, 0.2$ , and  $0.3$ . For all compounds investigated,  $\Gamma$  follows a universal square-root dependence at elevated temperatures,  $\Gamma = a\sqrt{T}$  with  $a = 0.17$ . Depending on the Zn concentration  $x$  the line-width passes through a minimum, which shifts to higher temperatures as  $x$  increases (see inset of Fig. 2). In traditional heavy  $f$ -electron compounds the residual quasielastic line-width for  $T \rightarrow 0$  usually is taken as the characteristic temperature  $T^*$  (Kondo lattice temperature). Such an interpretation would imply an increase of the Kondo lattice temperature upon the lattice expansion with increasing Zn concentration. The position of the minima of the relaxation rate is equivalent to the residual linewidth. Based on a  $1/N$

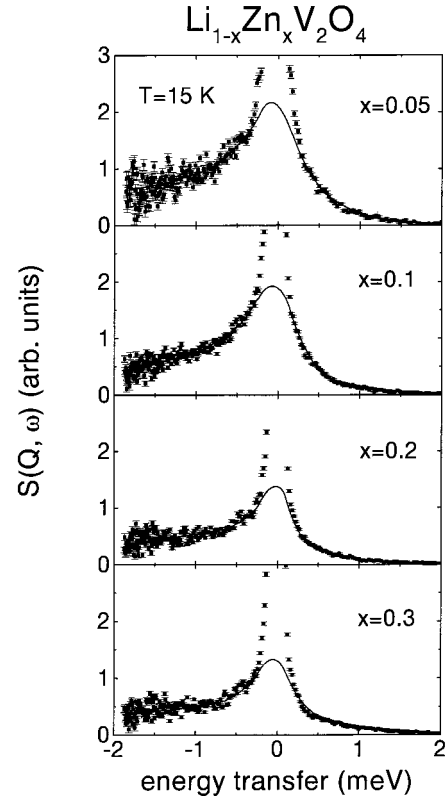


FIG. 1. Quasielastic scattering intensities of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  for  $x = 0.05, 0.1, 0.2$ , and  $0.3$  at  $T = 15 \text{ K}$ . The data have been corrected for background and detector efficiency and were fitted according to Eqs. (1) and (2) (solid line, see text).

expansion of the Anderson model, Cox *et al.*<sup>11</sup> proposed a universal behavior of the relaxation rate of both, pure Kondo and mixed valent compounds exhibiting a smooth minimum around  $T^*$ . Such a behavior has indeed been observed experimentally on the basis of neutron scattering and NMR experiments.<sup>12</sup> From our previous quasielastic neutron scattering study<sup>7</sup> on pure  $\text{LiV}_2\text{O}_4$  we have indication for the presence of strong antiferromagnetic spin fluctuations. A significant contribution of spin fluctuation in  $\text{LiV}_2\text{O}_4$  even at low temperatures within the heavy fermion state has also been obtained from the results of ESR and magnetic susceptibility measurements.<sup>13</sup> In particular, a continuous increase of the ESR linewidth at low temperatures as well as a strong magnetic field dependence of the low temperature susceptibility are not found in classical  $f$ -electron heavy fermion systems and both point to the presence of magnetic fluctuations.<sup>13</sup> The presence of significant magnetic fluctuations is also in accord with the results of  $\mu\text{SR}$  experiments.<sup>6</sup> The magnetic measurements by Ueda *et al.* revealed a spin-glass state in a large intermediate concentration regime  $0.1 \leq x \leq 0.9$  with freezing temperatures around  $T_F \approx 10 \text{ K}$ .<sup>9</sup> Magnetic and  $^7\text{Li}$  NMR measurements in our group<sup>15</sup> essentially confirmed the results by Ueda *et al.* and indicated the presence of antiferromagnetic fluctuations at low temperatures, revealing that these compounds are close to a magnetic instability. The spin-glass freezing temperature  $T_F$  increases with increasing Zn concentration [from  $\approx 8 \text{ K}$  for  $x = 0.1$  to  $\approx 15 \text{ K}$  for  $x = 0.3$  (Ref. 15)]. We therefore tentatively interpret  $\Gamma_{QE}(T \rightarrow 0)$  as the energy scale of antiferromagnetic spin fluctuations.

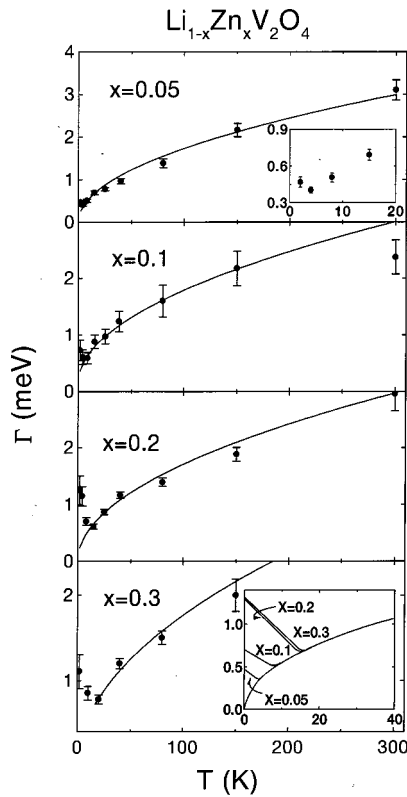


FIG. 2. Temperature dependence of the quasielastic linewidth of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ . The full line corresponds to  $\Gamma(T) = a\sqrt{T}$  with  $a = 0.17$ . The inset in the upper panel shows the quasielastic linewidth for the lowest temperatures to give evidence for the occurrence of a minimum for all concentrations investigated. In the inset of the lower panel, the temperature dependence of the quasielastic linewidth for the different concentrations is summarized in more detail on an expanded scale.

Spin-glass-like properties are also observed in the temperature dependence of the quasielastic intensity as shown in Fig. 3 for all compounds investigated. The temperature dependence of the quasielastic intensity exhibits, at first sight, a typical spin-glass behavior as found for example in  $\text{AuFe}$ .<sup>14</sup> With the given fixed instrumental resolution of  $\approx 100 \mu\text{eV}$  (corresponding to  $\approx 10^{-10}$  s) the quasielastic scattering intensity first grows upon decreasing temperature since more slow relaxation times fall into the time window of the instrument. After passing through a maximum  $T_{\text{max}}$ , the fast relaxation times within the quasielastic scattering window slow down as  $T_F$  is approached and the intensity becomes strongly suppressed. However, the magnitude of the temperature-dependent intensity changes point against a simple interpretation in terms of a canonical spin glass. In  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  the maximum is unusually well defined (as compared to prototypical spin-glass systems, e.g.,<sup>14</sup>  $\text{AuFe}$ ) and the subsequent decrease of the intensity for decreasing temperatures is stronger than that usually found in canonical spin glasses. In accordance with the present neutron scattering results, a very sharp maximum at  $T_{\text{max}}$  with a very high amplitude is also found in the spin-lattice relaxation rate  $1/T_1$  in  $^{57}\text{V}$  NMR experiments.<sup>15</sup> The increasing Zn concentration leads in fact to a suppression of the quasielastic scattering intensity at lowest temperatures. This behavior is illustrated in the inset of Fig. 3. At  $T = 1.8$  K and increasing  $x$ , the quasielastic

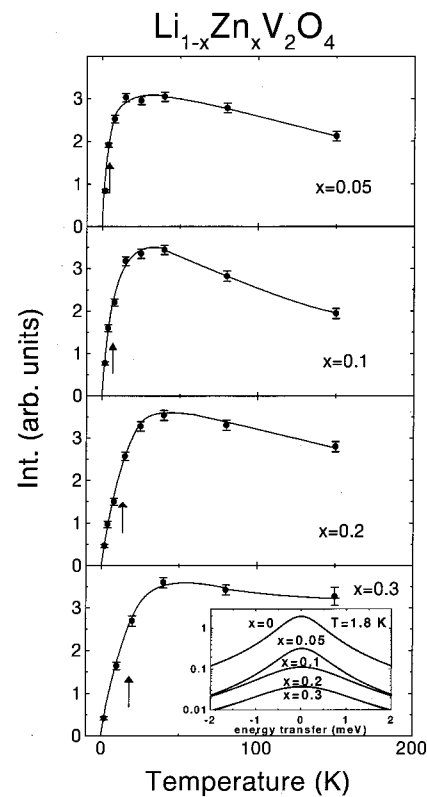


FIG. 3. Temperature dependence of the quasielastic intensity of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ . The solid line is only to guide the eye. The minima of the magnetic relaxation rate are indicated by arrows. The inset shows the concentration dependence of the quasielastic intensity of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  versus energy transfer at  $T = 1.8$  K on a semilogarithmic scale. Shown are the Lorentzian lines as resulting from the fit of the quasielastic scattering intensities [Eqs. (1) and (2)] when omitting the detailed balance factor.

response considerably decreases and becomes broader. Since the freezing temperature  $T_F$  increases with increasing Zn concentration, this strong suppression of the quasielastic scattering intensity at  $T = 1.5$  K reflects the increasing freezing out of magnetic fluctuations.

Also the square-root temperature dependence of the quasielastic linewidth cannot be explained by a spin-glass state alone. In pure  $\text{LiV}_2\text{O}_4$  various experimental techniques have established a low temperature heavy fermion behavior and a crossover to a different high temperature state above  $\approx 40$  K (a summary is given by Johnston<sup>16</sup>). Hence, the decrease of the quasielastic intensity in  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$  might tentatively be attributed to the onset of strong Kondo compensation effects below  $T \approx 40$  K. However, such a strong suppression of the intensity has never been observed in coherent  $f$ -electron heavy fermion compounds.

The occurrence of heavy fermion behavior in  $\text{LiV}_2\text{O}_4$  has been investigated by different groups performing local density approximation (LDA) band structure calculations.<sup>17–20</sup> All calculations result correctly in a metallic ground state with  $t_{2g}$  bands situated around the Fermi energy  $E_F$  and energetically well separated from the bands derived from the  $e_g$  orbitals. From band structure calculations<sup>18,20</sup> a density of states of  $D(E_F) \approx 7.2$  states/eV formula unit has been inferred, which is a factor 25 smaller than the experimental value derived from specific heat measurements. This discrep-

ancy indicates the importance of electronic correlations for the formation of the heavy fermion behavior in  $\text{LiV}_2\text{O}_4$ . Such correlation effects have been considered by Eyert *et al.*<sup>17</sup> on the basis of antiferromagnetic local V magnetic moments on the geometrically frustrated spinel lattice, leading to strong magnetic fluctuations that in turn give rise to a strong quasiparticle mass enhancement.

A different approach equivalent to an effective Anderson impurity model has been pursued by Anisimov *et al.*<sup>19</sup> The calculation results in a model with one  $3d$  electron per V ion well localized in a nondegenerate  $A_{1g}$  orbital and 0.5 electrons per V ion in a broad conduction band with primarily  $E_g$  symmetry and strong hybridization between them. This scenario can be reduced to a Kondo lattice model with a single site Kondo temperature of about 600 K. However, since there is an insufficient number of conduction electrons to screen all spins at this temperature, a coherent heavy fermion state is established at a much lower temperature  $T_{coh}$  (coherence temperature), in agreement with experiments. This phenomenon is known as exhaustion effect.<sup>22</sup> The discrimination among the different models describing the heavy fermion behavior in  $\text{LiV}_2\text{O}_4$  may be related to its high temperature state, which still has to be clarified. Whereas quasielastic neutron scattering<sup>7</sup> and NMR experiments<sup>5</sup> point towards an itinerant nearly ferromagnetic metal, high temperature NMR results were also interpreted in terms of a metal with almost localized magnetic moments.<sup>21</sup> Concerning the present Zn

doped compounds, the substitution of Li by Zn has different effects. First, local atomic disorder is introduced which may tend to more localized electronic states and an increasing effect of magnetic fluctuations. Second, the band filling increases with increasing Zn concentration which in turn may lead to an increasing Kondo temperature, at least in principle. Third, Zn doping is also accompanied by a lattice expansion, which necessarily leads to a weakening of the hybridization strength. These competing effects give rise to various possible ground state configurations. It should be noted that the Zn doping of  $\text{LiV}_2\text{O}_4$  leaves the local environment of the V ions unaltered. The local V-O bonds might display a rather different behavior than the observed overall lattice expansion in  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ . As described above, the present quasielastic neutron scattering results are in accordance with NMR<sup>15</sup> and magnetic measurements,<sup>9,15</sup> pointing towards a spin-glass transition with, however, somehow unusual low temperature properties. Magnetic fluctuations may play an important role for the low temperature behavior of  $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ . As mentioned by Johnston,<sup>16</sup> additional orbital and charge degrees of freedom may have to be taken into account to explain the physical properties of  $\text{LiV}_2\text{O}_4$  and evidently the Zn doped compounds.

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